

# **Interim Report on Task 1.1: Single-Phase Sample Production to Lawrence Livermore National Laboratory for Contract B345772**

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**U.S. Department of Energy**

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## Introduction

To properly interpret empirical data on the leaching and physical properties of the baseline ceramic, it is necessary but not sufficient to understand the corresponding behaviours of the main constituent phases, pyrochlore and brannerite. As a first step, the work has addressed making single phases containing only one actinide or Ce, and no neutron absorbers. This report addresses progress in making these phases.

## Experimental

To make single phases, it is normally necessary to maximise the precursor reactivity and homogeneity by using liquid precursors and wet-milling the calcines. Table 1 gives the details of the starting chemicals. After shear-mixing the alkoxide/nitrate precursors, drying at 110-400°C and calcining in an appropriate atmosphere at 750°C for 1 hour, the calcines were wet-milled in nylon jars with  $\text{ZrO}_2$  media for 16 hours and dried. Samples were then sintered in an appropriate atmosphere after pelletising, or hot-pressed in graphite dies. Characterisation was effected with SEM or XRD.

**Table 1: Raw materials used for the alkoxide batches.**

Element	Raw Materials for Alkoxide-route Batches (raw material, source, catalogue number)
Ca	99 % $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , Aldrich Chem. Co., 23712-4
Hf	99.99 % Hafnium n-butoxide, Gelest Inc.
Pu	Pu nitrate solution, (Pu-239) made by dissolving $\text{PuO}_2$ in 8M $\text{HNO}_3$ .
Th	$\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ , Merck, 1.08162
U	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , depleted (~ 0.318 % U235), BDH, Batch FF296, 10289
Ti	Titanium isopropoxide, HÜLS Troisdorf GmbH, 405514
Ce	99.9% $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , Aldrich chem. 23853-8

## Results

### Zirconolites

~ 99% yields of  $\text{CaZrTi}_2\text{O}_7$  and  $\text{CaHfTi}_2\text{O}_7$  were obtained by sintering at 1400°C for 96 hours (see Fig. 1 and 2)

### Pyrochlores

$\text{CaCeTi}_2\text{O}_7$ . The yield of this stoichiometric mixture was ~99% (see Fig. 3) when fired in air at 1200°C, giving densities of ~ 50% of theoretical. Lower temperatures failed to achieve sufficient reaction and higher temperatures produced perovskite via partial reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ . SRL workers have however produced Ce-rich materials at higher temperatures by allowing  $\text{Ce}^{3+}$  to (equally) inhabit the Ca and  $\text{Ce}^{4+}$  sites-for example using a  $\text{Ca}_{0.8}\text{Ce}_{1.2}\text{Ti}_2\text{O}_7$  stoichiometry in which 0.8 and 0.4 formula units of Ce are present in the +4 and +3 states respectively.

$\text{CaUTi}_2\text{O}_7$ . The best yield of this material so far has been 90 wt% using graphite-die hot-pressing at 1275°C (see Fig. 4). Sintering in argon has produced ~ 80% yield, but even melting in argon at 1500 or 1550°C has not improved the yield.

$\text{CaThTi}_2\text{O}_7$ . Zero yield of this phase has been obtained using air sintering at 1300-1500°C or even melting at 1550°C. The phases that did form were Th-brannerite and perovskite.

$\text{CaPuTi}_2\text{O}_7$ . A yield of ~ 75% has been obtained using air heating at 1450°C (see Fig. 5).

**Brannerites.**

$\text{CeTi}_2\text{O}_6$ . Near 100% yield was obtained by firing for 96 h at 1390°C (see Fig. 6), a temperature within ~ 20°C of the melting point which we independently determined. No evidence was found of any phase decomposition on cooling, using cooling rates of 5°C/min.

$\text{UTi}_2\text{O}_6$ . 98% yields ( see Fig.7) were obtained by argon sintering at 1400°C overnight or hot-pressing in graphite dies at 1250°C. For hot-pressing, it was necessary to mix 2 wt% of Ti metal with the calcine; after hot-pressing the ~ 100µm-thick layer adjacent to the graphite contained  $\text{UO}_2$  and  $\text{TiO}_2$  and was removed by mechanical means.

$\text{ThTi}_2\text{O}_6$ . Essentially 100% yield was obtained by sintering overnight in air at 1400°C.

$\text{PuTi}_2\text{O}_6$ . Air sintering at 1400°C produced a brannerite yield close to zero; 50 and 75% yields have been obtained by sintering overnight at 1500 and 1525°C (see Fig. 8) respectively. The extra phases in both cases were  $\text{PuO}_2$  and  $\text{TiO}_2$ .

**Final Remarks.**

Good progress has been made in the relatively difficult task of producing single actinide or Ce versions of pyrochlore and brannerite. Though we intend to carry out further work to increase the yields of U- and Pu-pyrochlores and Pu -brannerite, we expect that the second phase of this work will consist of making single phases containing both Pu and U as well as the neutron poisons Hf and Gd, and that this task will be easier than the work with the single actinide/Ce phases.

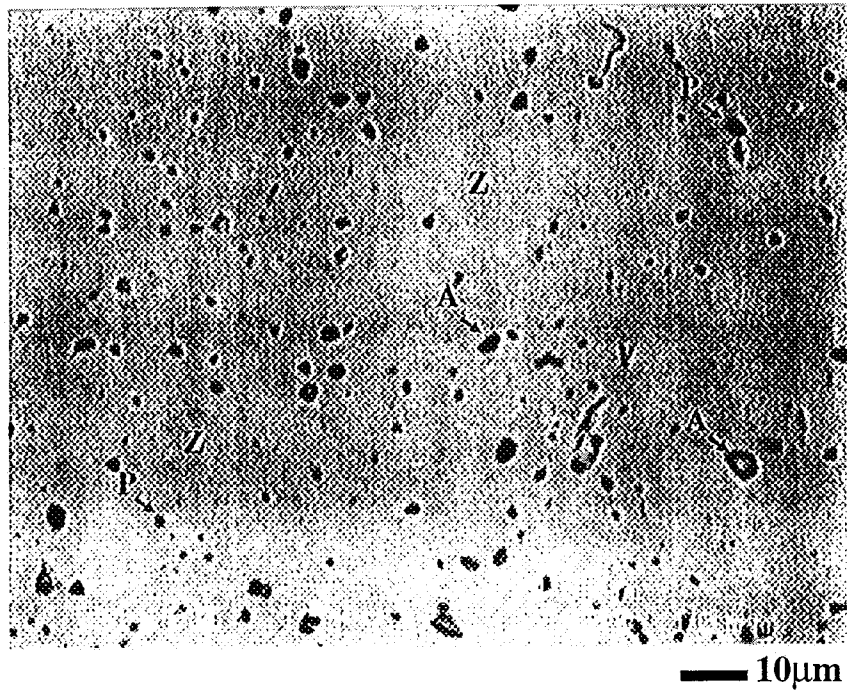


Figure 1 : Backscattered electron micrographs from zirconolite ( $\text{CaZrTi}_2\text{O}_7$ ), sintered 96 h at  $1400^\circ\text{C}$  in air. Z = zirconolite, P = perovskite and A = pore.

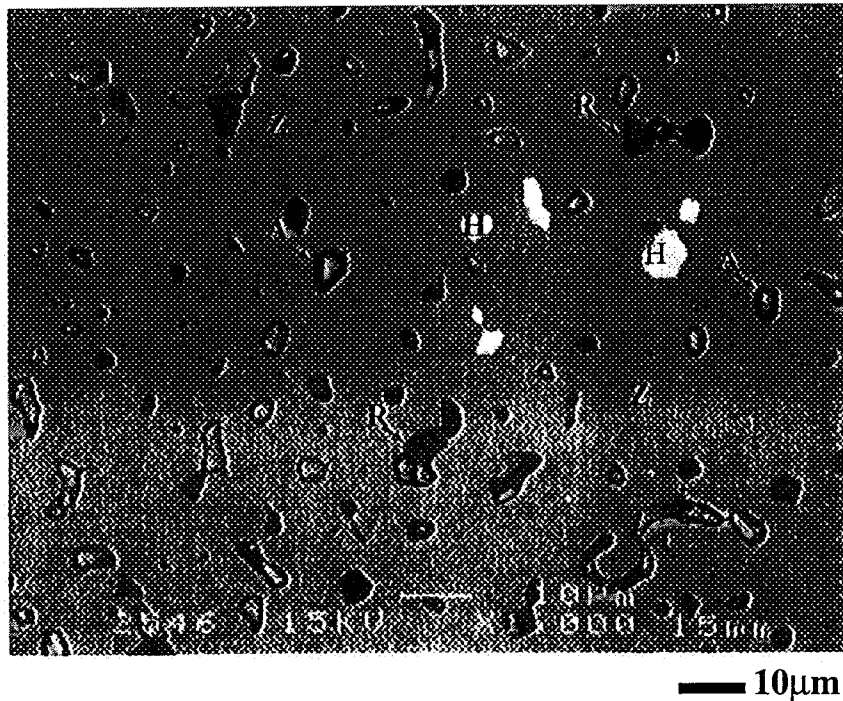


Figure 2 : Backscattered electron micrographs from zirconolite ( $\text{CaHfTi}_2\text{O}_7$ ), sintered 96 h at  $1400^\circ\text{C}$  in air. Z = zirconolite, H =  $\text{HfO}_2$ , R = rutile and A = pore.

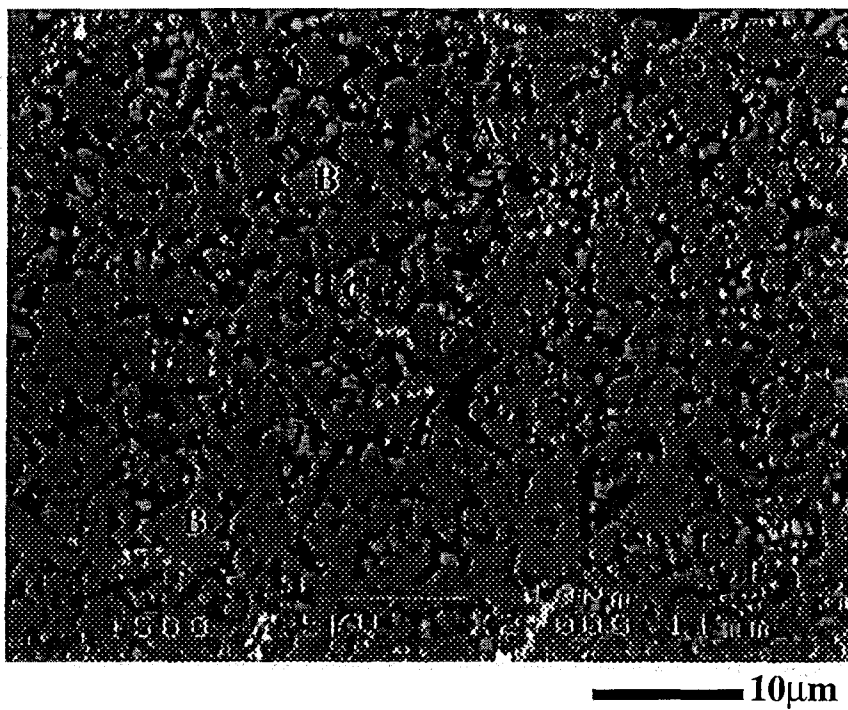


Figure 3 : Backscattered electron micrographs from pyrochlore ( $\text{CaCeTi}_2\text{O}_7$ ), sintered 96 h at 1200°C in air. B = pyrochlore, P = perovskite, C =  $\text{CeO}_2$  and A = pore.

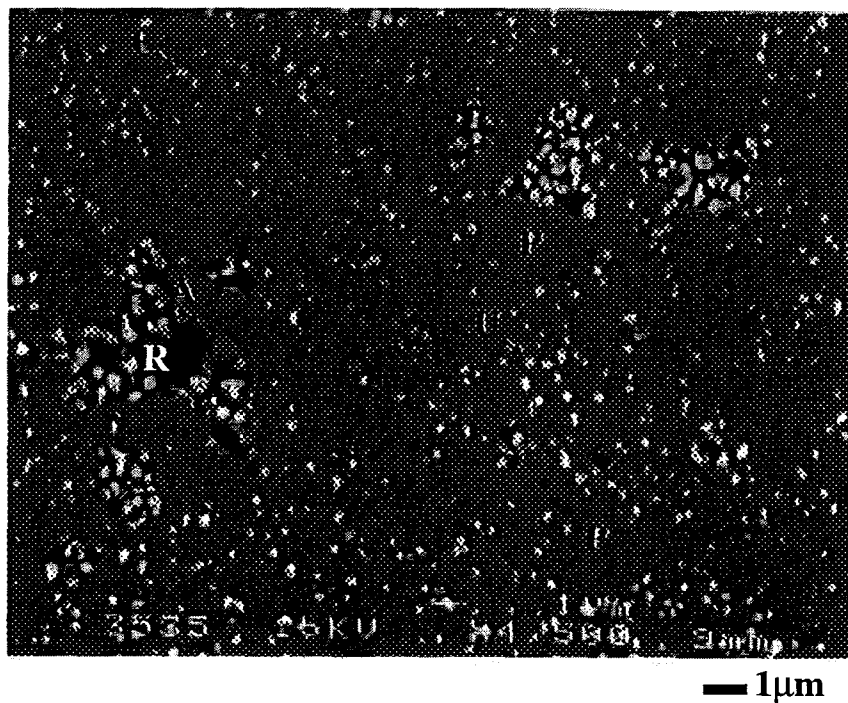


Figure 4 : Backscattered electron micrographs from pyrochlore ( $\text{CaUTi}_2\text{O}_7$ ), hot-pressed at 1275°C.  
P = pyrochlore, R = rutile, U =  $\text{UO}_2$  and A = pore.

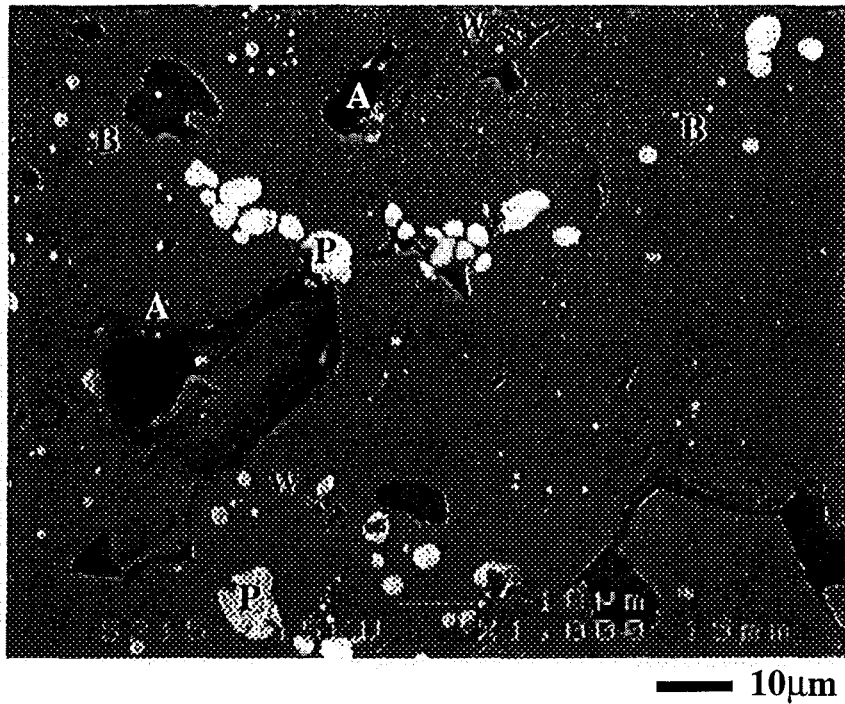


Figure 5 : Backscattered electron micrographs from pyrochlore ( $\text{CaPuTi}_2\text{O}_7$ ), sintered 16 h at  $1450^\circ\text{C}$  in air. B = pyrochlore, P =  $\text{PuO}_2$ , W = whitlockite from trace P impurity and A = pore.

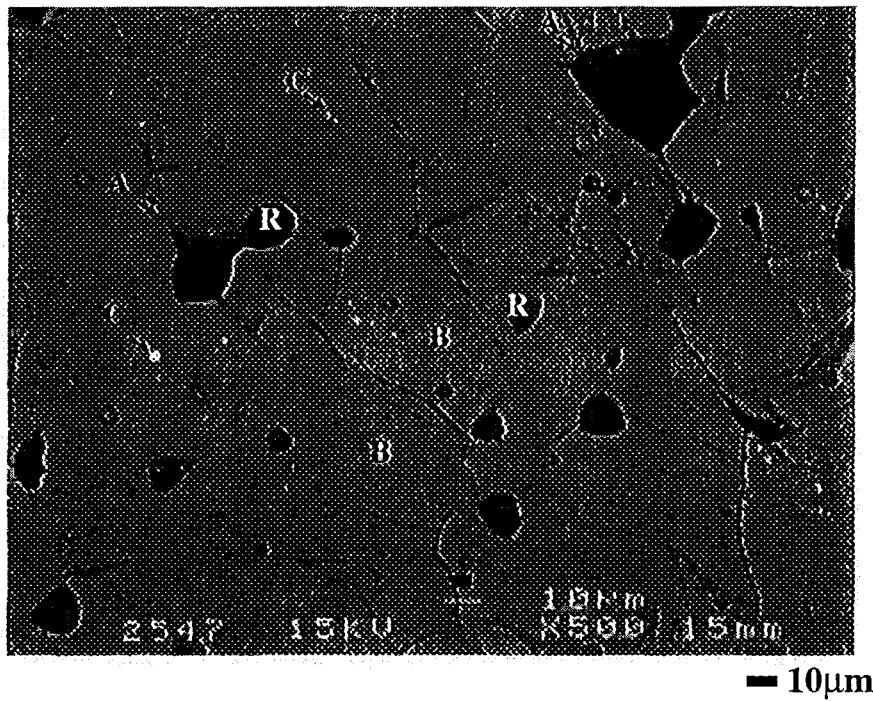


Figure 6 : Backscattered electron micrographs from brannerite ( $\text{CeTi}_2\text{O}_6$ ), sintered 96 h at  $1390^\circ\text{C}$  in air. B = brannerite, C =  $\text{CeO}_2$ , R = rutile and A = pore.

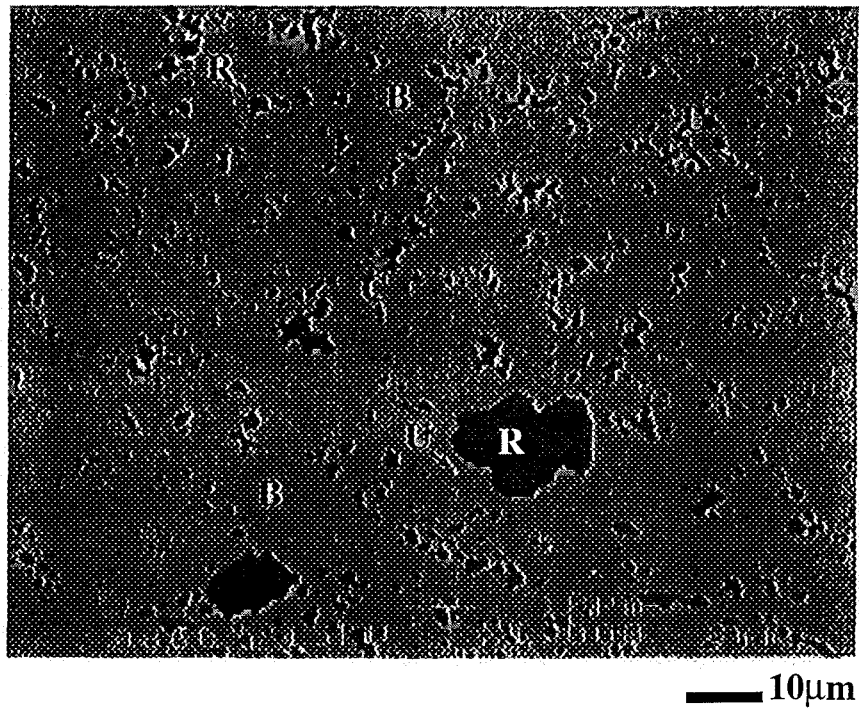


Figure 7 : Backscattered electron micrographs from brannerite ( $\text{UTi}_2\text{O}_6$ ), B = brannerite, R = rutile and U =  $\text{UO}_2$ .

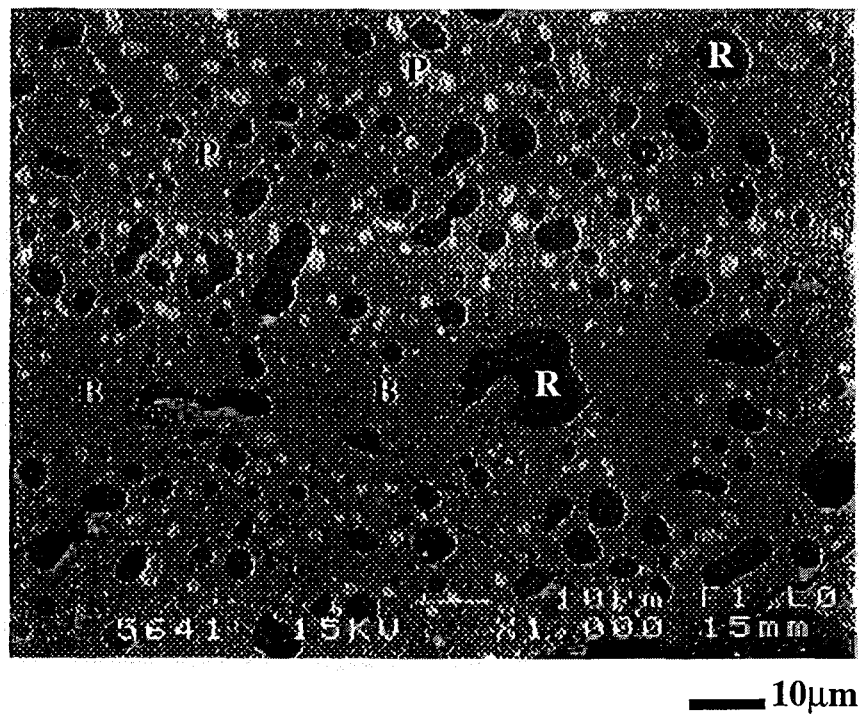


Figure 8 : Backscattered electron micrographs from brannerite ( $\text{PuTi}_2\text{O}_6$ ), sintered 16 h at 1525°C in air. B = brannerite, R = rutile and P =  $\text{PuO}_2$ .